removed by prolonged im-
acid ammonium thiosulfate
which has been added 15
acid per liter (½ oz. to 32
ld be used in a well-venti-
ause of the sulfur dioxide
e formed. After reduction
sh negatives thoroughly.

TREE, "Sulfide Stain," *P.S.A.*
752 (1947).

---

my first colored masks/sep
" transmutate
Only human

Chapter 14

PHOTOGRAPHIC DEVELOPERS. II. SILVER-DYE IMAGES

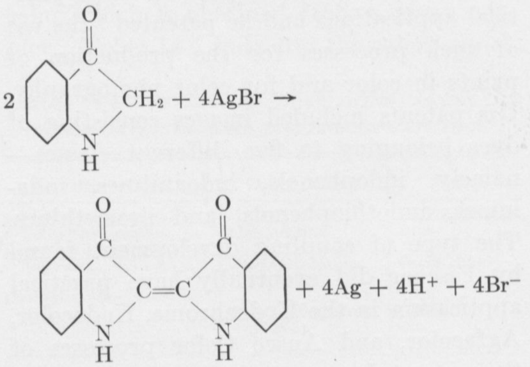
1952

Color Development

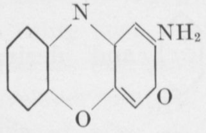
A number of developing agents used for developing a photographic latent image can, under certain conditions, deposit a colored image in addition to the silver image. Such color images become much more apparent when the silver image is removed by some agent such as Farmer's Reducer. The well-known developer, pyrogallol, when used without sulfite, gives a very strong brown "stain" image. This was first described by Liesegang[1] in 1895. Hydroquinone, catechol, amidol, and a number of other well-known developers also give stain or dye images. *o*-Aminophenol, 4-methoxynaphthol, hydrocoerulignone, indoxyl, and thioindoxyl are other agents which produce a dye image. The two latter agents were investigated by Homolka[2] in 1907.

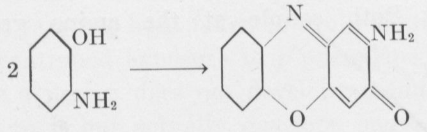
The exact structure of the "stain" or dye images produced by the normal developers such as pyrogallol and hydroquinone is not known, but it is composed of polymerization products of the oxidized developers and is closely related to the type of compounds known as humic acids.[3]

The reaction involved when indoxyl is used as a developer is perfectly straightforward. This substance is an intermediate of the dye *indigo*. During the development of a latent image indoxyl is oxidized to form the insoluble dye which is deposited simultaneously with the silver image according to the reaction



In a similar manner a number of other dye intermediates and leuco cases can be used as developers and form dye images.

The developer, *o*-aminophenol, is not a leuco base but is called a "self-coupling" developer. It forms the dye  as follows[4]



Dye-image formation by development with leuco bases or self-coupling developers has never become of any practical importance because of the poor color and instability of the images which can be formed or because of the poor latent-image developing properties of the compounds.

---

[1] Liesegang, *Phot. Arch.* **36**, 115 (1895).

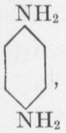
[2] Homolka, *Phot. Korr.* **44**, 55, 115 (1907); **51**, 256, 471 (1914), *Brit. J. Phot.* **54**, 136, 196, 216 (1907). Ermen, *Brit. J. Phot.* **70**, 47, 299 (1923).

[3] Tausch, *Thesis*, Dresden (1934).

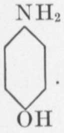
[4] Von Auwers, Borsche, and Weller, *Ber.* **54**, 1291 (1921).

In 1912 Fischer[5] found that certain agents, when added to *p*-phenylenediamine or *p*-aminophenol developer solutions, would cause the formation of a dye image accompanying the silver image. This was found to be due to the "coupling" of this added material to the oxidized developer and the material was called a "coupler." This nomenclature is still in use. Fischer realized that this principle had many practical applications and he patented[6] the use of such processes for the production of prints in color and for color photography. His patents included images consisting of dyes belonging to five different classes—namely, indophenols, indoanilines, indamines, indothiophenols, and azomethines. The type of coupling development found by Fischer did eventually have practical application in the Kodachrome, Kodacolor, Agfacolor, and Ansco Color processes of the present day.

Types of Dyes Formed by Coupling Development. There are two types of developers which can be used as coupling developers, derivatives of *p*-phenylenediamine

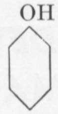


, and derivatives of *p*-aminophenol

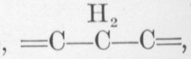


. Both couple at the amino group

so that the amino group in the *p*-aminophenol developers and one of the amino groups in the *p*-phenylenediamine developers must be unsubstituted. There are also two general types of couplers, phenols (or



napthols) , and materials containing an active methylene group,



$=C-\overset{H_2}{C}-C=$, a CH_2 group connected directly to two unsaturated carbon atoms. A *p*-phenylenediamine derivative couples with a phenol to form an indoaniline dye. A *p*-aminophenol derivative couples with a phenol to form an indophenol dye. The dyes formed when either *p*-phenylenediamine or *p*-aminophenol couples with an active methylene group are called azomethine dyes.

Couplers. The various elements and groupings that are combined in a compound which behaves as a coupler can be divided into two parts. The first of these is the color-forming part, which determines to a great extent (when used with a given developer) the color of the dye which is formed or the general region of the spectrum in which the dye will absorb light. The other parts of the material influence the stability of the dye formed, the solubility of the dye formed, as well as the solubility of the coupler itself in a developer solution, the diffusibility of the coupler

TABLE 14.1. EFFECT OF ADDED GROUPS ON THE COLOR FORMED FROM PHENOL AND NAPHTHOL COUPLERS (DEVELOPER DIETHYL-*p*-PHENYLENEDIAMINE)

Coupler	Group Added	Color
Phenol.		Greenish blue
o-Cresol.	CH_3	Blue
1,3,6-Xylenol.	Two CH_3	Deeper blue
α-Naphthol.		Blue
Dichloro-α-naphthol.	Two Cl	Cyan
Trichloro-α-naphthol. . . .	Three Cl	Green cyan
Pentachloro-α-naphthol. .	Five Cl	Green

---

[5] Fischer, *Brit. J. Phot.* **60**, 595, 712 (1913); **61**, 329 (1914).

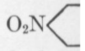
[6] U.S.P. 1,055,155; 1,079,756; 1,102,028. D.R.P. 253,335.

---

through an emulsion laye
sical characteristics. Th
be discussed further in a

All the phenol or naph
dyes which absorb light
the spectrum, thus giving
A few of the well-known
colors which they form
phenylenediamine are sh

Couplers which are p
acetyl compounds, and d
trobenzylcyanide,



coupled with diethyl-*p*-
give dyes with the major
green region of the spect
to magenta or orange dy
better known couplers
shown in Table 14.2.

TABLE 14.2. COUPLERS WHICH
WITH DIETHYL-*p*-PHEN

1-*p*-Nitrophenyl-3-meth
1-Phenyl-3-methyl-5-py
p-Nitrobenzylcyanide
Benzoylacetonitrile
Naphthoylacetonitrile

Couplers with the activ

$\overset{O}{\overset{\|}{-C-}}$

between two $-\overset{O}{\overset{\|}{C}}-$ grou
have their major absor
region of the spectrum a
or orange. A few of t
Table 14.3.

TABLE 14.3. COUPLERS WHICH
WITH DIETHYL-*p*-PHEN

Ethyl acetoace
Ethyl benzoyla
Acetoacetanilid
β-Naphthoylac
Diethyl malona

Thus, the cyan and b
by coupling development
indophenol dyes, and th
and magenta dyes are az

pers and one of the amino
p-phenylenediamine develop-
ısubstituted. There are also
'pes of couplers, phenols (or
I

and materials containing
,

ıylene group, $=C-\overset{H_2}{C}-C=$,
connected directly to two un-
on atoms. A *p*-phenylene-
ative couples with a phenol
ndoaniline dye. A *p*-amino-
ive couples with a phenol to
henol dye. The dyes formed
-phenylenediamine or *p*-ami-
les with an active methylene
ed azomethine dyes.

The various elements and
are combined in a compound
as a coupler can be divided
. The first of these is the
part, which determines to a
when used with a given de-
color of the dye which is
general region of the spec-
the dye will absorb light.
ts of the material influence
the dye formed, the solubil-
formed, as well as the solu-
oupler itself in a developer
diffusibility of the coupler

ECT OF ADDED GROUPS ON THE
FROM PHENOL AND NAPHTHOL
(DEVELOPER DIETHYL-*p*-
ENYLENEDIAMINE)

	Group Added	Color
....		Greenish blue
....	CH_3	Blue
....	Two CH_3	Deeper blue
....		Blue
ol.....	Two Cl	Cyan
hol....	Three Cl	Green cyan
hthol..	Five Cl	Green

---

through an emulsion layer, and other physical characteristics. These functions will be discussed further in a later section.

All the phenol or naphthol couplers form dyes which absorb light in the red end of the spectrum, thus giving cyan or blue dyes. A few of the well-known couplers and the colors which they form with diethyl-*p*-phenylenediamine are shown in Table 14.1.

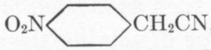
Couplers which are pyrazolones, cyanoacetyl compounds, and derivatives of *p*-nitrobenzylcyanide, , when coupled with diethyl-*p*-phenylenediamine, give dyes with the major absorption in the green region of the spectrum, thus leading to magenta or orange dyes. A few of the better known couplers of this type are shown in Table 14.2.

TABLE 14.2. COUPLERS WHICH GIVE A MAGENTA DYE WITH DIETHYL-*p*-PHENYLENEDIAMINE

1-*p*-Nitrophenyl-3-methyl-5-pyrazolone
1-Phenyl-3-methyl-5-pyrazolone
p-Nitrobenzylcyanide
Benzoylacetonitrile
Naphthoylacetonitrile

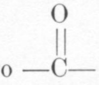
Couplers with the active methylene group between two  $-\overset{\overset{O}{\|}}{C}-$ groups give dyes which have their major absorption in the blue region of the spectrum and are thus yellow or orange. A few of them are shown in Table 14.3.

TABLE 14.3. COUPLERS WHICH GIVE A YELLOW DYE WITH DIETHYL-*p*-PHENYLENEDIAMINE

Ethyl acetoacetate
Ethyl benzoylacetate
Acetoacetanilide
β-Naphthoylacetone
Diethyl malonate

Thus, the cyan and blue dyes obtained by coupling development are indoaniline or indophenol dyes, and the yellow, orange, and magenta dyes are azomethine.

Coupling Developers.—The most important developers used for coupling to make a dye image are the substituted *p*-phenylenediamines. These may have one or two of the hydrogen atoms on one of the nitrogens substituted by methyl, ethyl, or other groups, and may have similar groups substituted in the benzene ring. However, one of the amino groups must remain unsubstituted in order for the developer to couple.

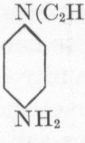
The exact structure of the developer influences the solubility of the dyes formed, the stability of the dyes, and the exact color which is obtained from a given coupler. Table 14.4 indicates the colors which are obtained when a few different developers are used with a given coupler.

TABLE 14.4. EFFECT OF DEVELOPING AGENT ON COLOR OBTAINED WITH DICHLORO-α-NAPHTHOL

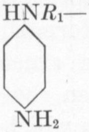
Developing Agent	Group Added	Color
p-Phenylenediamine.....		Pink or purple
p-Toluylenediamine.....	CH_3 on ring	Blue
Dimethyl-*p*-phenylenediamine............	Two CH_3 groups on N	Cyan Blue
Diethyl-*p*-phenylenediamine.............	Two C_2H_5 groups on N	Cyan

One of the chief disadvantages of the normal *p*-phenylenediamine developers is their strong tendency to cause a severe rash on human skin. In using such developers, extreme care must be exercised to avoid contact with the developer solution. Skin irritations have occurred after repeated use of such developers even when great care has been taken to avoid contact. On continued exposure to *p*-phenylenediamine a person does not develop an immunity to it but actually develops increased sensitivity.

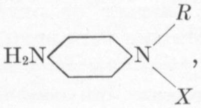
In recent years a number of patents have been granted describing new developers which are stated to be an improvement over the well-known dimethyl-*p*-phenylenediamine and diethyl-*p*-phenylenediamine. U.S.P. 2,210,843 describes a compound



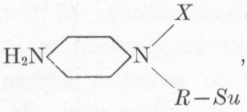
which has OH groups substituted in the two ethyl groups of diethyl-*p*-phenylenediamine. This compound is much more soluble in a developer solution than diethyl-*p*-phenylenediamine. U.S.P. 2,163,166 describes the compounds



, where R_1 is an alkylene or arylene group and Y is COOH or SO_3H, and the compounds



, where R represents H, alkyl, aryl, or hydroxy alkyl and X represents $—(CH_2CH_2O)_n—CH_2CH_2OH$. These compounds are stated to be more soluble than the usual color developers and to have greatly decreased toxic action on human skin. U.S.P. 2,193,015 describes the developer compounds

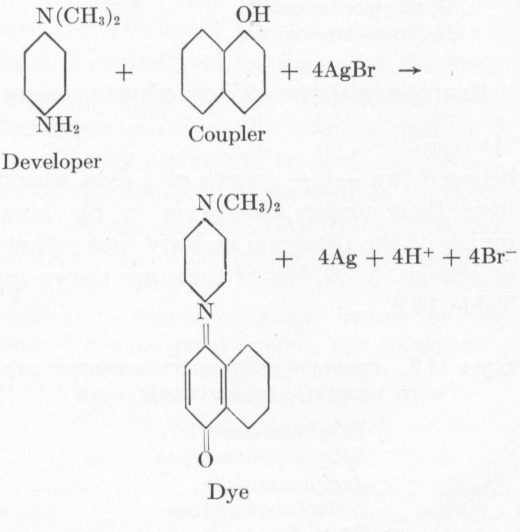


, where X represents hydrogen or alkyl, R represents alkylene, Su represents $—SO_2NH_2$, $—SO_2NHR'$, or $—NHSO_2R'$, where R' is hydrogen or alkyl. These compounds are also stated to be more soluble than normal color developers and much less toxic.

p-Aminophenol and substituted *p*-aminophenol can also be used as color developers. However, the solubility and the instability of the dyes formed from these developers make them unsatisfactory, and they have not been used in practice.

Developer Solution Ingredients. The constituents of coupling developer solutions are the coupler, the developer, an alkali which is usually required to dissolve the coupler and to make the developer sufficiently active, a buffer to preserve the alkalinity, a small amount of sulfite to act as preservative (the large amount of sulfite used in normal black-and-white developers usually interferes with the coupling reaction), bromide, and frequently an additional organic antifoggant. In some cases an organic solvent such as alcohol is used instead of an alkali for dissolving the coupler. Formulas for color-developer solutions which give cyan, magenta, and yellow dye images suitable for three-color work, as well as a variety of colors suitable for monochrome, have been published by Colton.[7]

Chemistry of the Coupling Development Reaction. During development or other methods of developer oxidation, the coupler reacts with the oxidized developer as follows:



Four molecules of silver bromide are reduced and four molecules of hydrobromic acid are formed. The reaction of a coupler

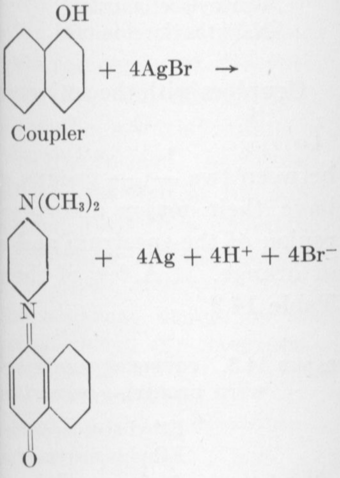
---

[7] Colton, *Photo-Technique* **1** (September 1939), 16.

r, the developer, an alkali
ly required to dissolve the
make the developer suffici-
uffer to preserve the alkalin-
ount of sulfite to act as pre-
large amount of sulfite used
k-and-white developers usu-
with the coupling reaction),
requently an additional or-
nt. In some cases an organic
alcohol is used instead of an
lving the coupler. Formulas
loper solutions which give
and yellow dye images suit-
-color work, as well as a
rs suitable for monochrome,
lished by Colton.[7]

f the Coupling Development

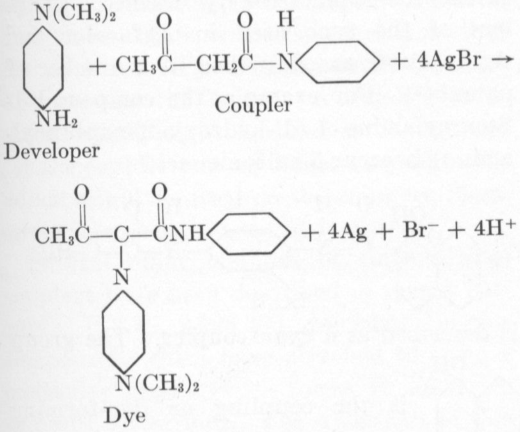
ring development or other
eloper oxidation, the coupler
e oxidized developer as fol-



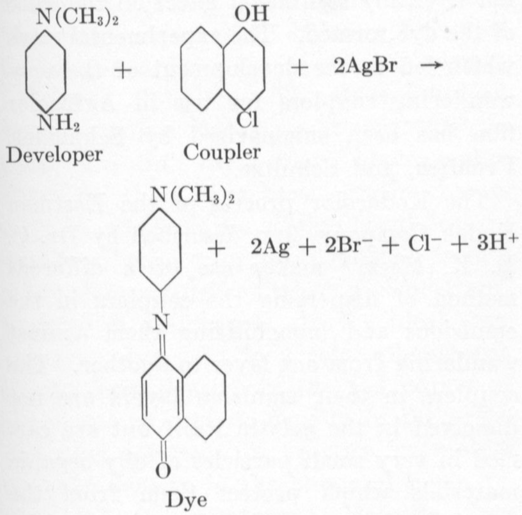
s of silver bromide are re-
ir molecules of hydrobromic
d. The reaction of a coupler

o-Technique 1 (September 1939),

with an active methylene group can be shown by a similar equation:

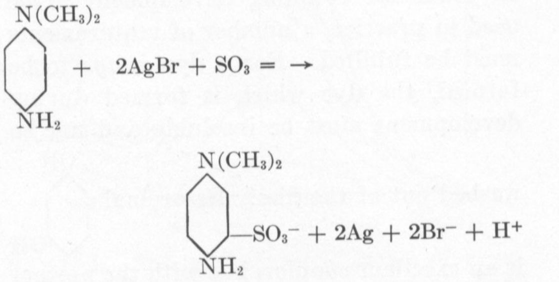


Certain phenol couplers have the coupling position occupied by a chlorine atom rather than the hydrogen. In this case the chlorine is split off during the coupling reaction and the same dye is formed as if the chlorine had not been present. For example,



Only two molecules of silver bromide are reduced, and two molecules of hydrobromic and one molecule of hydrochloric acid are released.

In practice, during the simultaneous development of a silver and dye image, reactions similar to those shown above take place but, in addition, some of the oxidized developer reacts with sulfite, which is normally included in all developer solutions. The reaction is



In addition, some developer is oxidized by the oxygen of the air, thus forming dye without the formation of silver, so that it is quite difficult to demonstrate experimentally the four-to-one ratio of the amount of silver and dye formed (or two-to-one in the case of chloro-substituted couplers) as indicated by the above equations.

The coupling reaction has been investigated by Flannery and Collins.[8] They used developers containing no sulfite but did not mention any specific steps taken to eliminate oxygen. For the cyan coupler, 2,4-dichloro-α-naphthol, they found 1.83 molecules of silver for every molecule of dye formed during the development reaction. This is in fair agreement with the value 2, which would be predicted from the equation for a chloro-substituted coupler. For the magenta coupler, 1-*p*-nitrophenyl-3-methyl-5-pyrazolone, 3.64 molecules of silver per molecule of dye were formed; and for the yellow coupler, furoyl-2-acet-2′,4′-xylidide, 3.4 molecules of silver per molecule of dye. These results are in fair agreement with the theoretical value of 4. The deviation of these results from the theoretical values must be attributed to experimental error rather than to any error in the terials vary with the wave length, the spectral energy characteristics of the light source are extremely important. In this respect also, it is highly desirable that the light source be comparable with one which is used in practical photography. A color temperature of 5400° K. has been accepted by international agreement as a standard when the characteristics of a sensitive material to sunlight are to be determined.

---

[8] Flannery and Collins, *Phot. J.* **86B**, 86 (1946).

In modern practice, negative materials are exposed also by incandescent tungsten lamps, fluorescent lamps, flash lamps, and gaseous discharge lamps. No standards for these have as yet been agreed upon, but a tungsten source with a color temperature of 2750° K. is widely used with positive materials. Any standard, of course, must be constant in intensity and in its spectral energy and both of these must be precisely known and reproducible.

Candles, and lamps burning liquid pentane, amyl acetate, and acetylene, have been employed as standards, but standardized incandescent electric lamps are used almost exclusively at the present time. It is necessary to calibrate such lamps accurately for luminous intensity and spectral distribution in a testing laboratory. Inasmuch as both of these factors depend upon the temperature of the filament, which in turn depends on the current flowing through the lamp, it is necessary to control with a high degree of precision the electric supply from which the lamp is operated.

Incandescent tungsten lamps of the type most suitable as a standard light source operate at color temperatures ranging from 2360° to 2800° K. It is necessary, therefore, to use a filter if radiation with the spectral energy characteristics of sunlight is required. For most purposes filters of dyed gelatin, such as the Wratten Nos. 78, 78A, 78AA, and 79, may be used; at the Seventh International Congress of Photography (London 1928), however, a tungsten lamp operating at a color temperature of 2360° K. and a liquid filter which had been proposed by Davis and Gibson of the U. S. Bureau of Standards was adopted.

Time-Scale Sensitometers. The usual method of producing a scale of exposures by varying the time (time scale) is by interposing, between the light source and the sensitive material, a continuously-moving, opaque plate with a series of apertures whose lengths vary in accordance with the differences in exposure desired. The apertures may be longitudinal in a rectangular plate which moves in a straight line, or angular openings in a circular disk which is rotated during the exposure (Fig. 17.1). The latter is by far the more popular method.

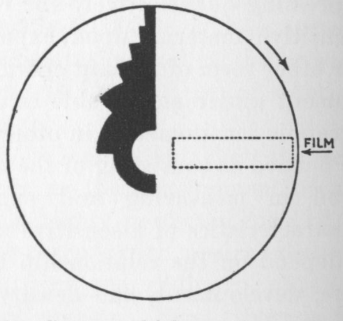


FIG. 17.1. Sector which produces a series of exposures to the power of two. The sensitive material occupies the space shown by the dotted line. The dark areas are slots in the disk.

Many different instruments of this type have been described in the literature. Practically all of these, however, have been designed by research workers, or in the laboratories of the manufacturers of sensitive materials, to meet certain specific requirements. In 1931 the Eastman Kodak Company placed a time-scale sensitometer on the market primarily for the motion picture laboratory, as the Eastman Sensitometer, Type IIb.

This instrument is shown in detail in Fig. 17.2.

L represents the standard lamp which is the source of illumination. A selectively absorbing filter, *F*, is placed in the path of the light coming from the lamp in order to modify its spectral composition to the desired quality. A plane mirror, *M*, reflects the light at right angles, thus illuminating the exposure plane, *EP*, in which the photographic material is placed. The rotating cylindrical shutter or drum, *D*, having 21 exposure slots of increasing length controls the time of exposure upon adjacent steps of the sensitive material. The platen, *PL*, when pulled down, serves to hold the film strips in the exposure plane during exposure.

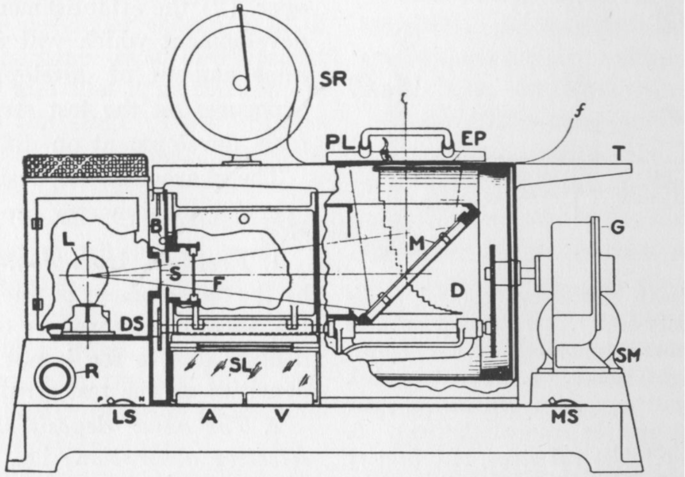


FIG. 17.2. Optical system of the Eastman IIb sensitometer (time-sca

The drum is driven at a constant angular velocity by a synchronous motor, *SM*. Through a reduction gear, *G*, the motor turns the drum at 12 r.p.m. when operating on a 60 cycle line, or at 10 r.p.m. on a 50 cycle line.

When the machine is started by throwing the master switch *MS*, the drum revolves continuously. Exposures are made by means of the shutter, *S*, operated by a one-turn mechanism. Upon pressure of the release button, *B*, this shutter opens while the

photographic material is prot
exposing radiation by the o
of the drum, and closes as so
in the drum have passed
plane.

Illumination Scale Sensit
illumination on different part
tive material may be varied
illumination scale of exposure
ing the distance between th
and the sensitive material fo
exposures, (2) by the use of
with apertures of various siz
the sensitive material being
other,[1] (3) by optical wedge
sisting of a stepped diagra
indrical, deforming lens,[2] (
a series of densities[3] in fron
tive material so that the i
varied in accordance with th

---

[1] See Eder, *Handbuch der Pho*

[2] Callier, *Phot. J.* **43**, 242 (1913
60, 972 (1913). McFarlane, *J.*
228, 445 (1939).

[3] The density scales used in such
made of pigmented gelatin accord
devised by Goldberg (*Brit. J. P*
(1910)), or are calibrated photog
such wedges.

only during the induction period. After the interstitial silver ions are all used up and the speck of silver has become large enough, the charged speck will actually pull some of the adjacent silver ions from the crystal lattice itself. These are replaced by some farther away, etc. However, this theory does not explain how the induction period varies with the charge on the developing ion.

The recent work of James has thrown so much light on the nature of the development process and has eliminated so much of the confusion resulting from the variety of results obtained on the effects of dyes, oxidation products, and the like, that it will be treated in its entirety as a separate unit.

James[19] first studies the rate of formation of silver from silver ions in solution by a variety of developing agents in the presence of specks of metallic silver. This parallels physical development. Reduction with hydroquinone and catechol is directly proportional to the concentration of the developing agent but is proportional to a fractional power of the silver ion concentration, indicating that the developer is not adsorbed to the silver specks but that the silver ions are adsorbed.

The role of adsorption in increasing the rate of chemical reactions can be clarified by quantum-mechanical principles.[20] Fig. 12.2 indicates the energy relations which might exist in a given reaction. For the reactants, silver ion and developer, to react in homogeneous solution they must go over a certain potential barrier as shown by the solid line. This requires a certain energy of activation, E_{hom}. The number of atoms which react will be a statistical function, depending upon the number which obtain this amount of energy from thermal agitation. However, when one or more of the reactants are adsorbed onto some active surface, the energy required for the reaction is decreased, as shown by the dotted line, so that much less energy is required for the reactants to get over the hump, or react. Under this condition the reaction will proceed at an increased rate.

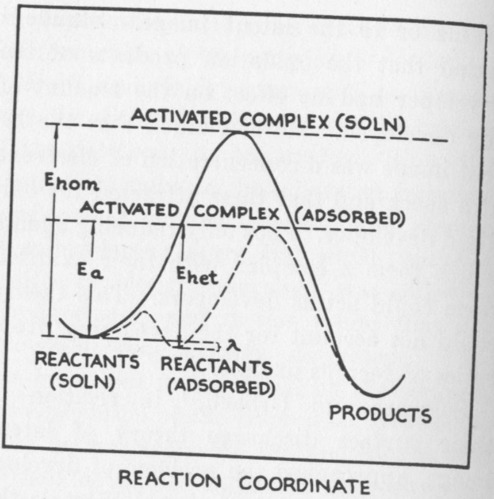
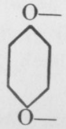


FIG. 12.2. Quantum-mechanical description of energies involved in a homogeneous reaction (E_{hom}) and in a similar reaction with absorption on a catalysis ($_{het}$).

In the case of development with paraphenylenediamine, the ratio is a fractional power of developer concentration and linear with silver ion concentration, indicating that the reaction proceeds by the adsorption of this developer.[21]

Development of ordinary emulsions in a variety of developers at different values of pH shows that the active ingredient of the developer is the ionized form of the developing agent. Ionization increases with pH; hence, development is more rapid at higher pH. For hydroquinone, the doubly ionized state



is the active agent; for elon and catechol, the singly ionized state; for hydroquinone monosulfonate, the triply ionized state; and for the derivatives of paraphenylenediamine, the neutral or un-ionized state. This variation in ionic character leads to the possibility of the classification of the developing agents into groups depending on their ionic charge. A study of the induction period of a number of developers shows that their behavior falls into a very neat pattern depending on the ionic charge,[22] as shown in Fig. 12.3. The curves, appropriately marked, show the course of the growth of density with the developers with 0, 1, 2, and 3 negative charges. The scale of the time of development has been adjusted for each developer so that the straight portions of all the curves have the same slope. For the strong developers the total time represented by the diagram is fairly short and for the weak developers it is fairly long, but with this adjustment all of the developers fall into this pattern. This change in induction period with ionic charge can be interpreted as indicating that the induction period is connected with the negatively charged barrier layer which surrounds the grains. The gr
charge on the developer the longe
to penetrate this layer.

The nature of the barrier layer
demonstrated by a number of exp
The presence of certain salts in a
frequently has a large effect on t
development, caused by the effe
salt on the charge layer contri
gelatin. Gelatin, being amphote
negative charge in solutions with
than its isoelectric point and a
charge at pH values lower than i
tric point. At values of pH gre
4.8, the isoelectric point of gelatin
ment with ferrous oxalate is slov
by the negatively charged gelati
layer. Addition of potassium
causes a large increase in the ra
velopment. At values of pH lo
4.8, the positively charged gela
increases the rate of development
rous oxalate. The addition of
nitrate to the developer with a
than 4.8 gives a large decrease in
of development. At a pH of 4.8,
tion of salt has no effect. The
effects of the salt additions at
values of pH indicate that the ne
tends to decrease the barrier la
tributed by gelatin. The salt ef
not occur in developers containin
charge action ingredient, such as
phenylenediamine derivatives.
James[23] states that this techniqu
used as a method for determinin
electric point of gelatin in an
This effect of neutral salt on dev
parallels the effect on certain dy
will not penetrate gelatin excep
presence of neutral salt.

The effect of certain dyes and
oxidation products on the charge
layer is due to their effect on the

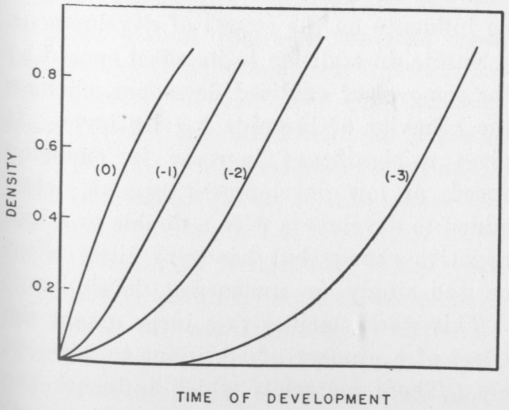


FIG. 12.3. Dependence of shape of time-density curve upon ionic charge of the developing agent.

---

[19] James, *J. Amer. Chem. Soc.* **61**, 648 (1939). James, *ibid.* **61**, 2379 (1939).

[20] James, *J. Chem. Ed.* **23**, 595 (1946).

[21] James, *J. Franklin Inst.* **240**, 15 (1945).

[22] James, *J. Franklin Inst.* **240**, 83 (1945).

[23] James, *J. Chem. Phys.* **12**, 453 (19

TABLE 12.1. COMPARISON OF DEVELOPING AGENTS AT MAXIMUM DEVELOPMENT

Agent	Relative Speed	Agent	Relative Speed
Hydroquinone (carbonate)	100.0	*p*-Amino-*o*-cresol	100.0
Catechol	97.8	D-19	93.3
Ferro-oxalate	95.5	Hydroquinone (caustic)	89.9
Elon	100.0	*p*-Aminophenylglycine	72.5
Elon monosulfonate	95.5	Hydroxylamine	72.5
Diaminodurene	95.5	*p*-Hydroxyphenylglycine	69.3
E-H	95.5	Ascorbic Acid	64.6

cine, and ferrous oxalate show a number of effects which do not occur with elon or the derivatives of paraphenylenediamine.

James[27] has also found that the maximum emulsion speed which can be obtained with a given emulsion and optimum development is practically the same for many developers. The formula which he chose was a caustic solution of the developer in the absence of air and sulfite, thus eliminating all but the essential ingredients. The caustic was chosen as the alkali because it gives complete ionization of all of the developers. Complete development was defined as that stage of development where the growth of density of fog was about equal to the growth of the image. The fog density involved was between 0.7 and 1.1, much more than occurs in practical cases. The time of development was different for the different developers. The emulsion speed for the various developers is shown in Table 12.1. Two standard developers, D19, and another elon hydroquinone developer, were included as a point of reference. Except for the last four in the table, all of which are fairly unusual developers, the speeds are not significantly different. It can be concluded that the basic mechanism of development is the same for all of these developers and that probably the size of the latent-image speck which is required to make a grain developable is about the same for all. This result must not be confused with normal practice where development is stopped far short of completion and a number of factors influence the rate of the development to that stage.

The practical advantage of a complex developer such as elon hydroquinone mixtures used in practice, according to James,[28] derives from the use of a developer with a single charge (elon) with a more powerful developer which has a double charge (hydroquinone). The one with the shorter induction period starts the grains developing and the more powerful one continues the development. On this principle he predicted that mixtures of hydroxylamine (one charge) and hydroquinone monosulfonate (three charges) would give greater densities than the sum of the two acting separately. His experiments upheld this. This result may be taken to indicate that the earlier held theory that elon and hydroquinone form a complex which is more active than either developer is not necessary to explain the behavior of the mixture.

The work of James does not make it possible to choose definitely between the two general types of theories of the mechanism of development which are held today. These are the "electrode" type which are based on the silver speck of the latent image accepting the electron from the developer and in turn passing it on to a silver ion of

---

[27] James, *J. Franklin Inst.* **239**, 41 (1945).

[28] James, T. H., Reference 26.

Amidol (Acrol, Dianol) 2.4-diaminophenol hydrochloride, $C_6H_3(OH)(NH_2).2HCl$.

Diaminophenol is an energetic developer with sodium sulfite alone. It develops, but more slowly, in an acid solution. The white or gray-white, needle-like crystals are readily soluble in water but oxidize rapidly without appreciable discoloration and solutions are no longer useful as developers within a few hours.[12]

Diaminophenol is now used principally for the development of chloride and bromchloride papers producing rich, cold-black tones. It is nearly always used alone, although diaminophenol-pyro has been recommended as a negative developer, the pyro functioning as a developer without an alkali in the presence of diaminophenol.

Catechol (Pyrocatechin, Kachin, Catechin. 1–2-dihydroxybenzene, $C_6H_4(OH)_2$.

Catechol is similar chemically to hydroquinone which is the corresponding para derivative. The oxidation products of catechol, like those of pyrogallol, tan the image:[13] this property has been utilized to produce gelatin relief images for three-color printing.

Catechol differs from other organic developers in functioning almost normally in the presence of hypo which makes it especially suitable for combined fixing and developing.

A combination of catechol and paraphenylenediamine has been introduced by Johnson and Sons Ltd. for fine grain development under the trade name of *Meritol*.

Glycin (Athenon, Kodurol, Monazol). N-(1.4-hydroxyphenyl) glycin. $HOC_6H_4 \cdot NHCH_2CO_2H$.

As a developer, glycin is slow but powerful. It is especially notable for the fine grain of the reduced silver and freedom from fog. Unlike other organic developers, glycin is not directly oxidized by air and it does not produce a stain image. It keeps well in solution and is well suited to continuous use in tanks. Today it is used chiefly in combination with paraphenylene diamine or metol for fine grain negative development and with hydroquinone for warm tones on chlorobromide and chloride papers.

Hydroquinone (Hydrochinon, Hydrokinone, Quinol). 1.4-dihydroxybenzene, $C_6H_4(OH)_2$.

Hydroquinone is a slow but powerful developer. The induction period is comparatively long, but the addition of density proceeds quite rapidly after the image has appeared, with the result that the arithmetical coefficient (Watkins factor) is low. In this respect, hydroquinone is almost the exact opposite of metol, diaminophenol, paraminophenol, etc.

Hydroquinone is used alone chiefly for work in which extreme contrast and density are required (process work). It may be used with the alkaline carbonates or the caustic alkalies, the latter producing greater density and contrast, or with paraformaldehyde. The activity of hydroquinone developers is greatly retarded by low temperature, becoming practically inert below

---

[12] Developing substances containing an amino, or a substituted amino group such as diaminophenol, paraminophenol, methyl paraminophenol (metol), oxidize readily and are commonly supplied in the form of a hydrochloride, sulfate or oxalate. For a discussion of the influence of the acid radical in developers, see Southworth, *Brit. J. Phot.* **84**, 711 (1937).

[13] Warnerke, B.P. 1436 (1881). Sanger Shepherd and Bartlett, B.P. 24,234 (1902). Koppmann, D.R.P. 309,193 (1913). Troland, B.P. 392,785 (1932). Starnes, B.P. 466,625 (1937).

Monomethyl paraminophenol: Dickins, U.S.P. 1,884,844; Whittaker, U.S.P. 1,993,253 and Bean, U.S.P. 2,315,932.

Paraminophenol: McDaniel, Schneider and Baller, *Trans. Elect. Chem. Soc.* **39**, 441 (1921).

55° F. At temper
excessive fog and
countered.

Other than for p
none is usually us
methyl paraminophe
ment one another
developer which fo
greatly superior to
because of its adap
most widely used d
time.

Metol (Elon, Enol,
Photol, Pictol,
methyl paramino
$(NHCH_3).\frac{1}{2}H_2S$

Metol is an ene
induction period i
metical coefficient h
image appears quic
trast increase more

The addition of
a developer with th
ducing characteris
density and contra
of hydroquinone.
metol-hydroquinone
are not simply the
the two agents. Th
as measured by eith
or contrast, is gre
when used togethe
two used separatel
that the increased
droquinone in con
formation of comp
bination introduce
as meto-quinone.
that the effect of a
quinone developer
tion period carryi
to the point at
becomes an active
quinone in this wa

---

[14] James, *J. Phot.*

f hypo which makes it espe-
for combined fixing and de-

ion of catechol and para-
ine has been introduced by
Sons Ltd. for fine grain de-
er the trade name of *Meritol.*

enon, Kodurol, Monazol).
xyphenyl) glycin. HOC_6H_4·
I.
er, glycin is slow but power-
ecially notable for the fine
reduced silver and freedom
ike other organic developers,
rectly oxidized by air and it
ice a stain image. It keeps
n and is well suited to con-
tanks. Today it is used
ination with paraphenylene
tol for fine grain negative
nd with hydroquinone for
chlorobromide and chloride

(Hydrochinon, Hydroki-
l). 1.4-dihydroxybenzene,

e is a slow but powerful
e induction period is com-
, but the addition of density
rapidly after the image has
the result that the arith-
nt (Watkins factor) is low.
hydroquinone is almost the
of metol, diaminophenol,
l, etc.
e is used alone chiefly for
xtreme contrast and density
process work). It may be
alkaline carbonates or the
the latter producing greater
ntrast, or with paraformal-
ctivity of hydroquinone de-
atly retarded by low tem-
ing practically inert below

55° F. At temperatures above 70° F. excessive fog and staining may be encountered.

Other than for process work, hydroquinone is usually used with metol (monomethyl paraminophenol). The two supplement one another admirably to form a developer which for general purposes is greatly superior to either alone and which because of its adaptability is by far the most widely used developer at the present time.

METOL (Elon, Enol, Genol, Monol, Monotol, Photol, Pictol, Rhodol, Veritol). 1.4-methyl paraminophenol sulfate HOC_6H_4-$(NHCH_3) . \frac{1}{2}H_2SO_4$.

Metol is an energetic developer. The induction period is short and the arithmetical coefficient high; in other words, the image appears quickly but density and contrast increase more slowly.

The addition of hydroquinone produces a developer with the energy and detail-producing characteristics of metol and the density and contrast-producing properties of hydroquinone. The properties of a metol-hydroquinone developer, however, are not simply the sum of the properties of the two agents. The speed of development, as measured by either the growth of density or contrast, is greater for the two agents when used together than the sum of the two used separately. It has been suggested that the increased activity of the metol-hydroquinone in combination is due to the formation of complexes similar to the combination introduced by A. and L. Lumiere as meto-quinone. It now appears, however, that the effect of adding metol to a hydroquinone developer is to reduce the induction period carrying development forward to the point at which the hydroquinone becomes an active developer.[14] The hydroquinone in this way makes its influence felt earlier than would otherwise be the case. The maximum effect is produced within a pH range of 9.0–10.5; as the pH decreases the part played by the hydroquinone becomes less and less.

Ordinarily the alkaline carbonates, or borates, are used, but metol alone will develop without an alkali and metol-sulfite formulas have been recommended (1) as compensating developers—for the development of subjects of extreme contrast, and (2) as fine-grain developers.[15]

PARAMINOPHENOL (Kodelon, Rodinal, Azol). 1.4-aminophenol $C_6H_4(OH)$-(NH_2) base $C_6H_4(OH)(NH_2) \cdot HCl$ hydrochloride.

When used with the alkaline carbonates, paraminophenol forms a rapid, soft working developer which is notably free from any tendency to produce development fog even at temperatures considerably above normal. It is, therefore, especially suitable for high-temperature development. In practice, however, paraminophenol is less popular than metol because it is more rapidly exhausted.

Highly concentrated developers of exceptional keeping properties may be prepared by adding paraminophenol to a solution of potassium metabisulfite and then adding sufficient sodium hydroxide to dissolve the precipitated free base. A developer of this type was patented and introduced commercially by Agfa as "Rodinal."[16] Numerous others have been introduced since.

---

[14] James, *J. Phot. Soc. Amer.* **9**, 62 (1943).

[15] Veldman, *Atelier* **35**, 30 (1928). Von Ehrhardt, *Amer. Phot.* **28**, 466 (1934). Wiegleb, *Schweiz. Phot.-Ztg.* **37**, 93 (1935). Henn and Crabtree, *J. Phot. Soc. Amer.* **10**, 727 (1944).

[16] On the preparation of "Rodinal type" developers see: Ermen, *Brit. J. Phot.* **67**, 611 (1920). Gray, *Brit. J. Phot.* **80**, 175 (1933). Willcock, *Brit. J. Phot.* **83**, 256 (1936).

PARAPHENYLENEDIAMINE (Diamine, Diamine P, Dianol, Diamine H (hydrochloride) P.D.H. 1,4-diaminobenzene $C_6H_4(NH_2)_2$ base $C_6H_4(NH_2)_2 \cdot 2HCl$ hydrochloride.

Para and possibly ortho-phenylenediamine are the only developers in which the graininess of the image is definitely lower than other developing agents. The fine grain is due to its solvent action on silver halide and its low reduction potential. These two factors prevent full development of the latent image, thus necessitating an increase in exposure as compared with more energetic developers and it is possible that development is largely of the character associated with physical development in which silver is deposited on the latent image from a silver-bearing solution.

The silver deposit is dichroic, i.e., black by transmitted light and cream-colored by reflected light. The printing density is greater than the visual density so that negatives which appear to be lacking in density and contrast may be of good printing quality.

Para-phenylenediamine is frequently combined with glycin, metol, or similar developers.[17]

Both the free base and the hydrochloride are strongly toxic and contact with the solutions should be avoided. The use of waterproof gloves is advised.

PYRO (Pyrogallol, Pyrol, Pyrox). 1.2.3-hydroxybenzene $(OH)_3C_6H_3$.

Pyro in recent years has been almost completely superseded by other developers and particularly by metol-hydroquinone. The behavior of pyro as a developer depends in a large measure on the dilution. Thus in a concentrated solution the induction period is relatively long but the image develops rapidly; in diluted solutions, on the other hand, the time of appearance is relatively short but density and contrast are added slowly.

Pyro oxidizes rapidly in solution, and while stock solutions with good keeping properties may be prepared with the addition of a relatively large quantity of an acid sulfite, pyro developers, as generally employed, have a useful life of only a few hours.

The developed image varies in color from a warm black to a yellowish black, depending upon the amount of sulfite or other preservative.

The photographic density and gamma of the pyro-developed image are higher than the visual density and contrast, the difference between the two, or the *color index*, depending primarily on the amount of preservative used.[18]

Development in pyro, particularly with small amounts of preservative, results in the tanning of the gelatin surrounding the silver of the image. This property has led to its use in the development of gelatin reliefs for three-color printing.

Pyro is used alone, in combination with metol to obtain a more energetic developer with a lower threshold value, and less frequently with other developing agents, such as glycin, diaminophenol, or paraphenylene. Used in combination with diaminophenol it develops without an alkali.[19, 20]

The Selectivity of Developing Agents. The relation between the development of

---

[17] Sease, *Camera* (Phila.) **47**, 1 (1933). Lowe, *Camera-Craft* **43**, 558 (1936).

Gallafent and E. I. Dupont patented (B.P. 580,237 of 1944) the combination of orthophenylene and aminophenols and polyhydroxybenzenes to form compounds useful as fine grain developers.

[18] Wilsey, *Brit. J. Phot.* **66**, 721 (1919).

[19] *Bunel Bull. Belge,* **44**, 151 (1922). Hall, *Amer. Phot.* **16**, 326 (1922).

[20] A number of methylated, ethylated or other substituted pyrogallols have been patented: Bayer, B.P. 10,721; Agfa, D.R.P. 155,568; Schultes, U.S.P. 2,017,295 and 2,057,451; Stockelbach, U.S.P. 2,037,742. See also: Emmerman, *Phot. Ind.* **36**, 1085 (1938); **34**, 896 (1936).

---

the image and th
measured by the r
tive densities, is
the developing ag
like all others, de
the conditions un
is used, the formu
velopment. Niet
between the fog d
potential of the d
velopment is carr
berstoff and Buk
found that devel
vided into two
which includes pa
cin, paraminophe
high-fog group w
includes bromhy
metol, pyro, hyd
none. Using a d
form composition,
agent, Shiberstoff
in the following
tivity; hydroqui
metoquinone, me
paraminophenol.
tivity decreases
ture.

**The Developir
Emulsion Speed.**
variation in emul
ent developing a
on the whole emu
the reduction po
agent but probab
cated.[23] Shibers
only insignificant
found no differe

---

[21] Nietz, *Theory*
trand Co., Inc., New

[22] Shiberstoff and
p. 101.

[23] Nietz, *Theory*
trand Co., Inc., Ne

[24] Shiberstoff and
p. 101.

[25] James, *J. Fran*

ıtrated solution the induc-
atively long but the image
; in diluted solutions, on
the time of appearance is
but density and contrast
.

rapidly in solution, and
tions with good keeping
e prepared with the addi-
ely large quantity of an
developers, as generally
useful life of only a few

image varies in color from
a yellowish black, depend-
nount of sulfite or other

hic density and gamma of
ed image are higher than
and contrast, the differ-
two, or the *color index,*
arily on the amount of
.[18]

n pyro, particularly with
f preservative, results in
e gelatin surrounding the
ge. This property has led
development of gelatin
color printing.
lone, in combination with
more energetic developer
shold value, and less fre-
r developing agents, such
phenol, or paraphenylene.
tion with diaminophenol
ut an alkali.[19, 20]

of Developing Agents.
ween the development of

. *Phot.* **66**, 721 (1919).
lge, **44**, 151 (1922). Hall,
(1922).
ethylated, ethylated or other
ls have been patented: Bayer,
, D.R.P. 155,568; Schultes,
nd 2,057,451; Stockelbach,
See also: Emmerman, *Phot.*
); **34**, 896 (1936).

---

the image and the development of fog, as measured by the relationship of the respective densities, is termed the *selectivity* of the developing agent. This characteristic, like all others, depends considerably upon the conditions under which the developer is used, the formula, and the degree of development. Nietz found no relationship between the fog density and the reduction potential of the developing agent when development is carried to completion.[21] Shiberstoff and Bukin,[22] on the other hand, found that developing agents may be divided into two classes: a low-fog group which includes paraphenylenediamine, glycin, paraminophenol, and catechol; and a high-fog group which, in increasing order, includes bromhydroquinone, chloroquinol, metol, pyro, hydroquinone and metoquinone. Using a developing solution of uniform composition, except for the developing agent, Shiberstoff placed developing agents in the following order of increasing selectivity; hydroquinone, chloroquinol, pyro, metoquinone, metol, glycin, catechol and paraminophenol. He also found that selectivity decreases with increased temperature.

The Developing Agent and Effective Emulsion Speed. Nietz found an 18-fold variation in emulsion speed between different developing agents and concluded that on the whole emulsion speed increased with the reduction potential of the developing agent but probably less than his data indicated.[23] Shiberstoff and Bukin [24] found only insignificant differences. James [25] also found no differences of importance among eleven developing agents, except in the early stages of development, but his results were obtained with a developer without sulfite and with development to completion, or to a fog density of 0.3, and thus do not duplicate the conditions under which the same developers are used in practice.

Undoubtedly, the capacity of a developing agent to develop the latent image fully depends upon the conditions under which it is used and is not a property of the developing agent alone. The sodium sulfite is a solvent of silver halide and, used in large quantities, most certainly affects the final result. Potassium bromide also lowers the effective emulsion speed early in development, but has been shown to result in higher speeds on prolonged development due to the reduction of fog. The pH of the solution may well be an important factor also.

Reduction Potential of Developing Agents. The relative reducing energy of a developing agent is known as its *reduction potential.* The reduction potential of a developing agent may be determined in one of three ways:

1. *The amount by which density is depressed with a given quantity of a restrainer such as potassium bromide.* For a given concentration of potassium bromide, under fixed conditions of development, the amount by which the density is reduced depends upon the ability of the developer to overcome the resistance of the soluble bromide. Hence, the concentration of bromide will be in direct proportion to the energy, or reduction potential, of the developing agent.[26]

2. *The amount of silver bromide reduced to silver by a given quantity of the developing agent.* By this method a given quantity of the developer is added to silver

---

[21] Nietz, *Theory of Development,* D. Van Nostrand Co., Inc., New York.

[22] Shiberstoff and Bukin, *Kino-Phot. Ind.* 1932, p. 101.

[23] Nietz, *Theory of Development,* D. Van Nostrand Co., Inc., New York.

[24] Shiberstoff and Bukin, *Kino-Phot. Ind.* 1932, p. 101.

[25] James, *J. Franklin Inst.* **240**, 41, (1945).

[26] Sheppard, *J. Chem. Soc.* (London) **39**, 530 (1906).

bromide, formed by precipitation in water, and the reduced silver is collected and measured. The reduction potential of the developing agent is then expressed in terms of the quantity of metallic silver produced from the reduction of the silver bromide.[27]

3. *Electrometric methods.* Electrometric methods have been utilized by Bredig, Matthews and Barmeier, Frary and Nietz, and more recently by Evans and Hanson.[28] The results obtained by the latter are quite different from earlier measurements made by the density depression method as will be evident from the following table in which the values from the density depression method, used by Nietz, are compared with those obtained by the electrometric method; the potentials given being measured against the standard saturated calomel reference cell.

	Reduction Potential	
Developing Agent	*Density Depression Method*	*Electrometric Method*
Diaminophenol	30	−0.434
Bromhydroquinone	21	−0.327
Monomethylparaminophenol sulfate	20	−0.308
Pyrogallol	16	−0.388
Dimethylparaminophenol sulfate	10	−0.293
Chlorhydroquinone	7.0	−0.335
Paraminophenol (HCl)	6.0	−0.291
Toluhydroquinone	2.2	−0.390
Hydroquinone	1.0 (standard)	−0.357
Paraphenylene diamine	0.3	—

The outstanding difference in the values obtained by the two methods is the much higher potential of hydroquinone with the electrometric method than with the older density depression method. It will be observed that the potential of hydroquinone, as measured by the electrometric method, is higher than that of monomethyl-paraminophenol (metol), while the difference in potential is greater, and in the opposite direction, when measured by the depression of density. The potentials, as measured electrometrically, do not correspond very well with the observed differences in the rate of development, or velocity constant, but are in fair agreement with the maximum densities obtainable with the various developing agents.

Differences in Developing Agents With Respect to Rate of Exhaustion. With all developers, there is a loss in activity with use. This loss in activity affects development in two ways: (1) longer development is required to reach a given degree of contrast or gamma, and (2) the lower densities are less fully developed tending to produce the effect of underexposure.

The effect of repeated use on density with different developing agents using a standard formula was investigated by Strauss who found that metol has the longest useful life, followed in order by paraminophenol, edinol, ortol, chloro-hydroquinone, glycin, pyrocatechin and, much worse than the others, pyro.

Ermen investigated the exhaustion of developers using the time of appearance on developing papers.[29] His results placed the different developing agents in the following order: metol (best), dimethylaminophenol, paraminophenol, metol-chlorohydroquinone, chloro-hydroquinone, and lastly hydroquinone.

Identification of the Principal Developing Agents. Methods of identifying the various organic developing agents have been described by Andresen,[30] Clarke,[31] Er-

---

[27] Andresen, *Phot. Korr.* **35**, 447 (1898). Valenta, *Photographische Chemie und Chemikalien-Kunde,* II, 506, Wm. Knapp, Halle a/S.

[28] Evans and Hanson, *J. Phys. Chem.* **41**, 509 (1937).

[29] *Brit. J. Phot.* **68**, 64 (1921).

[30] Andresen, Valenta, *Photographische Chemie und Chemikalienkunde,* Knapp, Halle a/S.

[31] Clarke, *J. Ind. and Eng. Chem.,* November, 1918; *Brit. J. Phot.* **65**, 499 (1918).